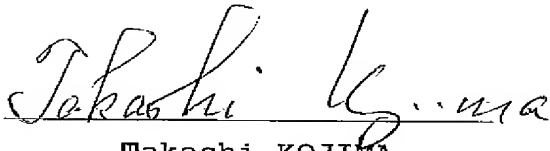


C E R T I F I C A T I O N

I, Takashi KOJIMA of Ginza Ohtsuka Bldg., 2F, 16-12, Ginza 2-chome, Chuo-ku, Tokyo, Japan, hereby certify that I am the translator of the accompanying certified official copy of the documents in respect of an application for a patent filed in Japan on the 9th of December, 2002 and of the official certificate attached thereto, and certify that the following is a true and correct translation to the best of my knowledge and belief.

Dated this 26th day of January, 2007

  
Takashi KOJIMA

(Translation)

PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: December 9, 2002

Application Number: Japanese Patent Application  
No. 2002-356171

[ST.10/C]: [JP 2002-356171]

Applicant(s): Shin-Etsu Chemical Co., Ltd.

September 17, 2003

Commissioner,  
Japan Patent Office      Yasuo IMAI  
(sealed)

Certificate No. 2003-3076279

2002-356171

[Paper] APPLICATION FOR PATENT

[Reference Number] 14570

[Application Date] December 9, 2002

[Destination] The Commissioner of the Patent Office  
Shinichiro OTA

[International Patent Classification]  
H01F 07/02

[Inventor]  
[Address] c/o Takefu Plant,  
Shin-Etsu Chemical Co., Ltd.,  
2-1-5, Kitago,  
Takefu-shi, Fukui-ken  
[Name] Noriaki HAMAYA

[Applicant]  
[Identification Number] 000002060  
[Name] Shin-Etsu Chemical Co., Ltd.

[Agent]  
[Identification Number] 100079304  
[Patent Attorney]  
[Name] Takashi KOJIMA

[Agent]  
[Identification Number] 100114513  
[Patent Attorney]  
[Name] Saori SHIGEMATSU

[Agent]  
[Identification Number] 100120721  
[Patent Attorney]  
[Name] Katsushige KOBAYASHI

[Official Fee]  
[Deposit Account Number] 003207  
[Amount of Fee] 21000

[List of Documents Attached]

[Document]	Specification	1
[Document]	Abstract	1

[Necessity of Proof]	Yes
----------------------	-----

2002-356171

[SPECIFICATION]

[TITLE OF THE INVENTION] Heat Resistant Coated Member

[CLAIMS]

5 [Claim 1] A heat resistant coated member comprising a substrate having a coefficient of linear expansion of at least  $4 \times 10^{-6}$  (1/K) and a layer comprising rare earth-containing oxide coated thereon.

10 [Claim 2] The heat resistant coated member of claim 1 wherein the coating layer comprises at least 80% by weight of a rare earth oxide and the balance of another metal oxide which is mixed, combined or laminated therewith.

15 [Claim 3] A heat resistant coated member comprising a substrate having a coefficient of linear expansion of at least  $4 \times 10^{-6}$  (1/K) and a layer consisting of rare earth oxide coated thereon.

20 [Claim 4] The heat resistant coated member of any one of claims 1 to 3 wherein the rare earth oxide is mainly composed of an oxide of at least one element selected from the group consisting of Dy, Ho, Er, Tm, Yb, Lu, and Gd.

[Claim 5] The heat resistant coated member of any one of claims 1 to 4 wherein said coating layer has a thickness of 0.02 mm to 0.4 mm.

25 [Claim 6] The heat resistant coated member of any one of claims 1 to 5 wherein said coating layer has been formed by thermal spraying.

30 [Claim 7] The heat resistant coated member of any one of claims 1 to 6 which is used in the sintering of a powder metallurgical metal, cermet or ceramic material in vacuum or an inert or reducing atmosphere.

[DETAILED EXPLANATION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

35 This invention relates to a heat resistant coated member which is used especially in the sintering or heat treatment of powder metallurgical metal, cermet or ceramic materials in vacuum or an inert or reducing atmosphere.

[0002]

[Prior Art]

In general, the powder metallurgy or ceramic manufacturing process involves firing or sintering and heat treatment steps. The specimen that is to become a product is set on the tray. Since the specimen can react with the tray material to invite a deformation or compositional shift or introduce impurities into the product, there are many cases where products are not fired or sintered in high yields. There are many ways for preventing the reaction of the tray with the product, as described above. For example, an oxide powder such as alumina or yttria or a nitride powder such as aluminum nitride or boron nitride is used as the placing powder. Alternatively, such an oxide or nitride powder is mixed with an organic solvent to form a slurry, which is coated or sprayed to the tray to form a coating on the tray for preventing the tray from reacting with the product. On use of placing powder, however, some of the placing powder will deposit on the product. The slurry coating procedure must be repeated every one or several sintering steps because the coating peels from the substrate (tray).

[0003]

To solve these problems, JP-A 2000-509102 proposes to form a dense coating on the surface of a tray by a thermal spraying technique.

[0004]

Although the thermally sprayed coating of this patent publication is effective for preventing reaction with the product, there is a likelihood that the coating readily peels off due to thermal degradation at the interface between the coating and the tray substrate by repeated thermal cycling. It is thus desired to have a coated member in which the oxide coating does not peel from the substrate even when subjected to repeated thermal cycling, that is, having heat resistance, corrosion resistance, durability and non-reactivity.

[0005]

[Patent Document 1]

JP-A 2000-509102

[0006]

5 [Problem to be Solved by the Invention]

The present invention has been done in order to improve the above circumstances. An object of the present invention is to provide a coated member which exhibits excellent heat resistance, corrosion resistance,  
10 non-reactivity, and durability which means that the coating scarcely peels off upon repeated thermal cycling, when used in the sintering or heat treatment of powder metallurgical metal, cermet or ceramic materials in vacuum or an inert or reducing atmosphere.

15 [0007]

[Means for Solving the Problem and Embodiment of the Invention]

The present inventors have earnestly studied in order to attain the above object. As a result, it has been found  
20 that a heat resistant coated member in which a substrate having a coefficient of linear expansion of at least  $4 \times 10^{-6}$  (1/K) is coated with a rare earth-containing oxide exhibits heat resistance, durability (the coating scarcely peels off upon repeated thermal cycling) and non-reactivity to a  
25 product, when used in the sintering or heat treatment of a powder metallurgical metal, cermet or ceramic material in vacuum or an inert or reducing atmosphere. The present invention has thus been completed.

[0008]

30 Accordingly, the present invention provides the following heat resistant coated member.

(1) A heat resistant coated member comprising a substrate having a coefficient of linear expansion of at least  $4 \times 10^{-6}$  (1/K) and a layer comprising rare earth-containing oxide  
35 coated thereon.

(2) The heat resistant coated member of (1) wherein the coating layer comprises at least 80% by weight of a rare

earth oxide and the balance of another metal oxide which is mixed, combined or laminated therewith.

(3) A heat resistant coated member comprising a substrate having a coefficient of linear expansion of at least  $4 \times 10^{-6}$  (1/K) and a layer consisting of rare earth oxide coated thereon.

(4) The heat resistant coated member of any one of (1) to (3) wherein the rare earth oxide is mainly composed of an oxide of at least one element selected from the group consisting of Dy, Ho, Er, Tm, Yb, Lu, and Gd.

(5) The heat resistant coated member of any one of (1) to (4) wherein said coating layer has a thickness of 0.02 mm to 0.4 mm.

(6) The heat resistant coated member of any one of (1) to (5) wherein said coating layer has been formed by thermal spraying.

(7) The heat resistant coated member of any one of (1) to (6) which is used in the sintering of a powder metallurgical metal, cermet or ceramic material in vacuum or an inert or reducing atmosphere.

[0009]

The following is the detailed description of the invention.

The heat resistant coated member of the present invention have a layer of rare earth-containing oxide coated on the substrate.

[0010]

The heat resistant coated member of the present invention is intended for use in the sintering or heat treatment of powder metallurgical metals, cermets or ceramics in vacuum or inert or reducing atmosphere to form a product. It is recommended that the combination of coating oxide and substrate be varied and optimized in accordance with the temperature of heat treatment, the temperature of sintering and the atmosphere. The coated member of the invention is particularly effective as crucibles for melting metal or as jigs for fabricating and sintering various types



of complex oxides. Examples of such jigs include setters, sagers, trays and molds.

[0011]

A substrate having a coefficient of linear expansion  
5 of at least  $4 \times 10^{-6}$  (1/K) is used as the substrate for forming  
a coated member having heat resistance, corrosion resistance  
and durability for use in the sintering or heat treatment of  
powder metallurgical metals, cermets or ceramics. The  
preferred substrate has a coefficient of linear expansion of  
10  $4 \times 10^{-6}$  to  $50 \times 10^{-6}$  (1/K), more preferably  $4 \times 10^{-6}$  to  $20 \times 10^{-6}$   
(1/K). As used herein, the coefficient of linear expansion  
is a coefficient of thermal expansion of a solid as is well  
known in the art. It is given by the equation:

$\alpha = (1/L_0) \times (dL/dt)$  wherein  $L_0$  is a length at  $0^\circ\text{C}$ , and  $L$  is a  
15 length at  $t^\circ\text{C}$ . It is noted that the coefficient of linear  
expansion used herein is an average measurement over a  
temperature range of 20 to  $100^\circ\text{C}$ .

[0012]

Rare earth-containing oxides which are effective as  
20 the protective coating for preventing reaction with powder  
metallurgical products, cermet products or ceramic products  
generally have a coefficient of linear expansion of  $4 \times 10^{-6}$  to  
 $8 \times 10^{-6}$  (1/K) in a temperature range of 20 to  $400^\circ\text{C}$ . When a  
coating is formed on a substrate from such a rare  
25 earth-containing oxide by a thermal spraying technique, it  
is important that the coefficient of linear expansion of the  
substrate be equal to or greater than that of the rare  
earth-containing oxide coating. Such adjustment restrains  
the coating from delamination by thermal cycling. This is  
30 due to the anchoring effect known in the thermal spraying  
art.

[0013]

Selection of a substrate having a higher coefficient  
of linear expansion than a coating enhances the anchoring  
35 effect. It should be understood that the type of substrate  
material which can be used is limited in certain cases

because the melting point and atmosphere resistance of the substrate must also be taken into account depending on the firing or sintering temperature and atmosphere or the heat treating temperature and atmosphere to which powder metallurgical products, cermet products or ceramic products are subjected.

[0014]

For example, a carbon substrate is a typical substrate to be used in a vacuum atmosphere at 1,400 to 1,600°C. The carbon substrate is widely used for sintering because it has a low density or a light weight, and a high strength and is easily machinable. When carbon is used as a substrate to be covered with an oxide coating, the substrate should preferably have a coefficient of linear expansion of at least  $4 \times 10^{-6}$  (1/K). If the coefficient of linear expansion is less than  $4 \times 10^{-6}$  (1/K), the anchoring effect becomes weak, with a likelihood for the thermally sprayed coating to peel upon thermal cycling to a high temperature of at least 1,400°C.

[0015]

The coefficient of linear expansion of a carbon substrate is closely related to the density of the carbon substrate and the particle size and crystallinity of primary particles of which the carbon substrate is made. Even when the substrate has a high density, the coefficient of linear expansion varies with the particle size and crystallinity of primary particles of which the substrate is made. Thus, a mere choice of a high density carbon substrate is insufficient because the anchoring effect is weak if the coefficient of linear expansion is less than  $4 \times 10^{-6}$  (1/K), with a likelihood for the thermally sprayed coating to peel upon thermal cycling to a high temperature of at least 1,400°C.

[0016]

When a transparent ceramic such as YAG is sintered, treatment within a temperature range of 1,500 to 1,800°C in

a vacuum, an inert atmosphere or a weakly reducing atmosphere tends to give rise to reactions between the substrate material and the coating oxide and to reactions between the coating oxide and the product on account of the elevated temperature. It is therefore important to select a substrate and coating oxide combination that discourages such reactions from arising. At temperatures above 1,500°C in particular, when carbon is used in the substrate, aluminum and rare-earth elements tend to form carbides in a vacuum or a reducing atmosphere. Under such conditions, it is desirable to use a coated jig in which a molybdenum, tantalum or tungsten substrate is combined with a rare-earth-containing oxide as the oxide coating.

[0017]

The substrate has a density of preferably at least 1.5 g/cm<sup>3</sup>, and especially 1.7 to 20 g/cm<sup>3</sup>.

[0018]

The coated members of the present invention have a layer of rare earth-containing oxide coated on the substrate.

[0019]

The rare earth-containing oxide used herein is an oxide containing a rare earth element or elements; that is, an element selected from among those having the atomic numbers 57 to 71. In this case, the substrate is preferably coated with an oxide of at least one rare earth element selected from among Dy, Ho, Er, Tm, Yb, Lu and Gd, more preferably an oxide of Er, Tm, Yb, Lu or Gd. This is because oxides of light to medium rare earth elements ranging from La to Tb undergo transitions in their crystalline structures below 1,500°C, by which transition the coating becomes brittle and liable to peel off to contaminate the product or the apparatus, or some oxides are reactive with carbon.

[0020]

An oxide of a metal selected from Group 3A to Group 8 elements may be mixed, combined or laminated with the rare

earth oxide in an amount of up to 20% by weight, and especially up to 18% by weight. More preferably, an oxide of at least one metal selected from among Al, Si, Zr, Fe, Ti, Mn, V, and Y is used.

5           The oxide coating may consist of the rare earth oxide.

          The rare earth-containing oxide used herein is preferably in the form of particles having an average particle size of 10 to 70  $\mu\text{m}$ . The coated member is preferably prepared by plasma spraying or flame spraying a  
10   rare earth-containing material in an inert atmosphere such as argon to deposit a coating of rare earth-containing oxide on the substrate. If necessary, the substrate is surface treated by a suitable technique such as blasting prior to the thermal spraying.

15           [0021]

          The coating of rare earth-containing oxide has a thickness of 0.02 mm to 0.4 mm, more preferably 0.1 mm to 0.2 mm. At less than 0.02 mm, there is a possibility that on repeated use of the coated member, the substrate may  
20   react with the material being sintered. On the other hand, at more than 0.4 mm, thermal shock within the coated oxide film may cause the oxide to delaminate, possibly resulting in contamination of the product.

          [0022]

25           The heat resistant coated member thus produced may be used to effectively heat-treat or sinter powder metallurgical metals, cermets and ceramics at a temperature of up to 1,800°C, and preferably 1,500 to 1,700°C, for 1 to 50 hours. The heat treatment or sintering atmosphere is  
30   preferably a vacuum or an inert or reducing atmosphere.

          [0023]

          Exemplary metals and ceramics are any one obtained by sintering or heat treatment and include chromium alloys, molybdenum alloys, tungsten carbide, silicon carbide,  
35   silicon nitride, titanium boride, silicon oxide, rare earth-aluminum complex oxides, rare earth-transition metal alloys, titanium alloys, rare earth oxides, and rare earth

complex oxides. The coated members of the invention, typically in the form of jigs, are effective especially in the production of tungsten carbide, rare earth oxides, rare earth-aluminum complex oxides, and rare earth-transition  
5 metal alloys. More specifically, the coated members of the invention are effective in the production of magnetically permeable ceramics such as YAG and cemented carbides such as tungsten carbide, the production of Sm-Co alloys, Nd-Fe-B alloys and Sm-Fe-N alloys used in sintered magnets, and the  
10 production of Tb-Dy-Fe alloys used in sintered magnetostrictive materials and Er-Ni alloys used in sintered regenerators.

[0024]

Examples of suitable inert atmospheres include argon  
15 and nitrogen (N<sub>2</sub>) atmospheres. Examples of suitable reducing atmospheres include hydrogen gas.

[0025]

[Effect of the Invention]

In addition to having a good heat resistance, the  
20 coated member of the invention also has a good corrosion resistance, non-reactivity and durability which means that the coating scarcely peels off upon repeated thermal cycling, and can therefore be effectively used for sintering or heat-treating powder metallurgical metals, cermets or  
25 ceramics in a vacuum, an inert atmosphere or a reducing atmosphere.

[0026]

[EXAMPLE]

The following examples and comparative examples are  
30 provided to illustrate the invention, and are not intended to limit the scope thereof.

[0027]

[Examples and Comparative Examples]

There were furnished matrix materials: carbon,  
35 molybdenum, tantalum, tungsten, aluminum, stainless steel, sintered alumina and sintered yttria (the latter two being oxide ceramics) having different coefficients of thermal

expansion as shown in Table 1. The matrix materials were machined into substrates having dimensions of 50×50×5 mm. The surface of the substrate was roughened by blasting, following which rare earth-containing oxide particles were plasma-sprayed in argon/hydrogen onto the substrate surface, thereby forming a spray coated member with a rare earth-containing oxide coating of 200 μm thick.

[0028]

It is noted that the coefficient of thermal expansion of substrate shown in Table 1 was measured on a prism specimen of 3×3×15 mm in an inert atmosphere according to a differential expansion method using a thermomechanical analyzer TMA8310 (Rigaku Denki K.K.). The measurement is an average coefficient of thermal expansion over the temperature range of 20 to 100°C.

[0029]

In Example 7,  $\text{Yb}_2\text{O}_3$  powder and  $\text{Zr}_2\text{O}_3$  powder were mixed in a  $\text{Yb}_2\text{O}_3$  :  $\text{Zr}_2\text{O}_3$  weight ratio of 80 wt%: 20 wt% to form a mixture, which was sprayed. In Example 8, a powder in which 90 wt% of  $\text{Yb}_2\text{O}_3$  was chemically combined with 10 wt% of  $\text{Al}_2\text{O}_3$  was used in spraying. In Example 9,  $\text{Yb}_2\text{O}_3$  powder was sprayed to form a coating of 100 μm thick, after which a  $\text{Y}_2\text{O}_3$  coating of 100 μm thick was formed thereon by spraying.

[0030]

These spray coated members based on the substrates having different coefficients of thermal expansion were set in a carbon heater furnace. The furnace was evacuated to vacuum, heated in a nitrogen atmosphere up to 800°C at a rate of 400°C/h, evacuated to vacuum again, and heated in a vacuum atmosphere of  $10^{-2}$  Torr up to a predetermined temperature at a rate of 400°C/h. After holding at the temperature for a certain time, the heater was turned off. Argon was introduced at 1000°C, after which the furnace was cooled down to room temperature at a rate of 500°C/h. This heating and cooling cycle was repeated 10 times. After the thermal cycling test, the coated members were observed under

a microscope with a magnifying power of 100× to see whether the sprayed coating peeled from the substrate. The results are shown in Table 2.

[0031]

5

Table 1

	Sprayed coating composition	Substrate material	Substrate density (g/cm <sup>3</sup> )	Substrate coefficient of thermal expansion (1/K)
Example 1	Er <sub>2</sub> O <sub>3</sub>	C	1.70	4.2×10 <sup>-6</sup>
Example 2	Er <sub>2</sub> O <sub>3</sub>	C	1.75	5.2×10 <sup>-6</sup>
Example 3	Er <sub>2</sub> O <sub>3</sub>	C	1.82	6×10 <sup>-6</sup>
Example 4	Yb <sub>2</sub> O <sub>3</sub>	C	1.70	4.2×10 <sup>-6</sup>
Example 5	Yb <sub>2</sub> O <sub>3</sub>	C	1.75	5.2×10 <sup>-6</sup>
Example 6	Yb <sub>2</sub> O <sub>3</sub>	C	1.82	6×10 <sup>-6</sup>
Example 7	Yb <sub>2</sub> O <sub>3</sub> +Zr <sub>2</sub> O <sub>3</sub> (80 wt%:20 wt%)	C	1.82	6×10 <sup>-6</sup>
Example 8	Yb <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub> (90 wt%:10 wt%)	C	1.70	4.2×10 <sup>-6</sup>
Example 9	upper Y <sub>2</sub> O <sub>3</sub> / lower Yb <sub>2</sub> O <sub>3</sub> (100 μm/100 μm)	C	1.75	5.2×10 <sup>-6</sup>
Example 10	Yb <sub>2</sub> O <sub>3</sub>	Mo	10.2	5.3×10 <sup>-6</sup>
Example 11	Yb <sub>2</sub> O <sub>3</sub>	Ta	16.6	6.3×10 <sup>-6</sup>
Example 12	Yb <sub>2</sub> O <sub>3</sub>	W	19.1	4.5×10 <sup>-6</sup>
Example 13	Yb <sub>2</sub> O <sub>3</sub>	Al	2.7	23.1×10 <sup>-6</sup>
Example 14	Yb <sub>2</sub> O <sub>3</sub>	stainless steel	8.2	14.7×10 <sup>-6</sup>
Example 15	Yb <sub>2</sub> O <sub>3</sub>	sintered Al <sub>2</sub> O <sub>3</sub>	3.97	8.6×10 <sup>-6</sup>
Example 16	Yb <sub>2</sub> O <sub>3</sub>	sintered Y <sub>2</sub> O <sub>3</sub>	4.50	9.3×10 <sup>-6</sup>
Comparative Example 1	Er <sub>2</sub> O <sub>3</sub>	C	1.74	1.5×10 <sup>-6</sup>
Comparative Example 2	Yb <sub>2</sub> O <sub>3</sub>	C	1.74	1.5×10 <sup>-6</sup>
Comparative Example 3	Yb <sub>2</sub> O <sub>3</sub>	C	1.60	2.5×10 <sup>-6</sup>

[0032]

Table 2

	Test temp. (°C)	Holding time (hr)	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	Observation after thermal cycling test of 10 cycles
Example 1	1400	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 2	1400	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 3	1400	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 4	1500	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 5	1500	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 6	1500	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 7	1500	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 8	1500	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 9	1500	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 10	1600	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 11	1600	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 12	1600	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 13	500	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 14	900	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 15	1400	4	○	○	○	○	○	○	○	○	○	○	not peeled
Example 16	1500	4	○	○	○	○	○	○	○	○	○	○	not peeled
Comparative Example 1	1400	4	○	○	×	×	×	×	×	×	×	×	peeled in 3rd cycle
Comparative Example 2	1500	4	○	○	○	○	○	×	×	×	×	×	peeled in 6th cycle
Comparative Example 3	1500	4	○	○	○	○	○	○	○	○	×	×	peeled in 9th cycle



[0033]

The spray coated members of Examples 1 to 16 remained unchanged after the thermal cycling test of 10 cycles in vacuum in a carbon heater furnace relative to before  
5 treatment, with no evidence of peeling of the coating from the substrate observed. In the coated members of Comparative Examples 1 to 3, the coating peeled from the substrate during the thermal cycling test. It is demonstrated that when a coating is sprayed on a substrate  
10 having a coefficient of thermal expansion of at least  $4 \times 10^{-6}$  (1/K), the coated member is durable in that the coating do not peel from the substrate during thermal cycling.

2002-356171

[ABSTRACT]

[Means for Solution]

A heat resistant coated member comprising a substrate having  
5 a coefficient of linear expansion of at least  $4 \times 10^{-6}$  (1/K) and a  
layer comprising rare earth-containing oxide coated thereon.

[Effect]

In addition to having a good heat resistance, the coated  
member of the invention also has a good corrosion resistance,  
10 non-reactivity and durability which means that the coating scarcely  
peels off upon repeated thermal cycling, and can therefore be  
effectively used for sintering or heat-treating powder  
metallurgical metals, cermets or ceramics in a vacuum, an inert  
atmosphere or a reducing atmosphere.

15 [Selected Drawing] none